

# Nonequilibrium Volumetric Response of Shocked Polymers

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Consider a high molecular weight polymer. Each polymer molecule may contain hundreds to even millions of atoms. The backbone of the molecular structure is the polymer chain. For amorphous polymers these chains typically form complex networks. It is common for the polymer to have physical entanglements, chemical cross linkages, or both. Because of the inherent complexity at the molecular level, it is relatively easy to drive an equilibrated polymer into a nonequilibrium state by application of a simple mechanical deformation. The externally applied deformation can be shear, or more generally deviatoric, but also volumetric in nature.

It is widely recognized that the chain mobility is the physical quantity that governs how successful a polymer will be at relaxing back into an equilibrium state for the deformed system. The chain mobility is the ability of the polymer molecules to locally rearrange themselves, to bring the deformed structure back into a state of equilibrium. Obviously the available thermal energy is an important factor in this process. For temperatures far above the glass transition temperature  $T_g$ , the chain mobility is high and a polymer is expected to relax quickly back into a state of equilibrium. However, below  $T_g$  the chain mobility is low and the polymer system may effectively become frozen into a long-lived metastable nonequilibrium state.

In any mechanical experiment, besides the loading rate, two other characteristic times are important when considering polymer relaxation—the total duration of the experiment and the experimental resolution over which the measurements are taken. Thus, first consider a simple low rate uniaxial compression experiment used to measure the polymer's stress-strain behavior. For discussion it is useful to make the gross simplification that molecular relaxation processes can be categorized as fast, intermediate, and slow. This categorization corresponds approximately to a

prototypical shear relaxation spectrum characteristic of many amorphous polymers [1]. Fast processes involve only few atoms (or chain segments) in single molecules and are associated with high frequency vibrational modes. At the other extreme are the relaxation modes associated with the collective motion of many chain segments involving many neighboring polymer molecules. For an entangled polymer, relaxation times for these processes are correspondingly very long. Between these extremes are the numerous intermediate rate relaxations. When a uniaxial compression experiment is done the system is immediately driven out of equilibrium. Fast relaxations occur so rapidly that such modes fully relax long before the first measurement is taken. However, long-lived modes will continue over the duration of the experiment.

The process of polymer relaxation and its effects on the mechanical behavior is encompassed in the theory of polymeric viscoelasticity, and because the viscoelastic response is associated mainly with the deviatoric response, the relevant theory is deviatoric viscoelasticity. When the range of strain rates is limited, as in the case of laboratory uniaxial compression experiments, volumetric viscoelasticity may typically be ignored. One then invokes an equilibrium equation of state (EOS) to describe the volumetric behavior. A more fundamental reason for ignoring volumetric viscoelasticity is that for small volumetric changes, it is primarily the high frequency vibrational modes (those associated with fast relaxation processes) that are likely to be compatible with the volumetric deformation, and thus likely to be excited. As long as the experiment is long and the resolution is low, relaxation of these modes will not be observable.

Next, consider a plate impact experiment where, by the action of a shock introduced into the system, the polymer will rapidly transition from an initial equilibrium state to a high-pressure shocked state. The duration of these experiments is typically microseconds (before release waves interrupt the shocked state), and the resolution is on the order of nanoseconds. For this case we argue that volumetric relaxations from the nonequilibrium shocked state to the equilibrium shocked state, i.e., volumetric viscoelasticity, must not be ignored.

To appreciate the deviation of the shocked state from the equilibrium state, we first formulate the equilibrium EOS. Here we will define the equilibrium EOS as that which is obtained using slow measurements, i.e., those lasting minutes to hours. Typical measurements satisfying this criterion are the calorimetric-measured specific heat and dilatometry-measured specific volume. Both of these are available in the literature—a tabulated specific heat for polymethyl-methacrylate (PMMA) is listed in the Advanced Thermal Analysis System (ATHAS) database [2], and specific volume isobars are reported in [3]. To use this data a semi-empirical expression for the Gibbs free energy is parameterized. The resulting Gibbs free energy (Fig. 1), and isothermal bulk modulus (Fig. 2) are shown for illustration.

Because the Gibbs free energy describes a complete EOS, the equilibrium Hugoniot can be calculated by satisfying the Rankine-Hugoniot jump conditions. The resulting equilibrium Hugoniot is plotted using the shock and particle velocities and compared with the shock experimental Hugoniot of [4]. It is immediately obvious from Fig. 3 that the two Hugoniots show major discrepancies. We speculate that this difference is due to the volumetric response of a polymer being rate dependent; while the equilibrium EOS measurements have deformation rates occurring over inverse minutes to hours, the shock measurements have a characteristic deformation rate of  $10^6$ - $10^7$  s<sup>-1</sup>. We thus assert that the bulk relaxation function should increase by about a factor of two as PMMA is shocked from equilibrium up to shock loading rates, i.e., volumetric viscoelasticity must not be ignored.

To include nonequilibrium effects, a Helmholtz free energy is written as the sum of an equilibrium,  $A_e$ , plus a nonequilibrium contribution coming from the deviatoric "D" and bulk "B" parts [5]:

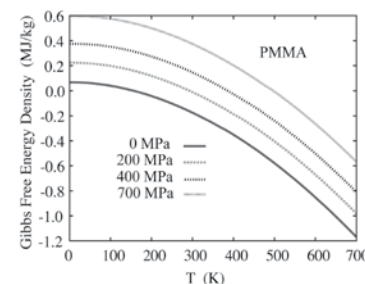
$$\begin{aligned} \rho A(\varepsilon_v, e_{ij}^e, T, \dot{\varepsilon}_v, \dot{e}_{ij}^e) &\approx \rho A_e(\varepsilon_v, e_{ij}^e, T) \\ &+ \int_0^t \int_0^t G_D(t_1, t_2; t) \frac{de_{ij}^e(t_1)}{dt_1} \frac{de_{ij}^e(t_2)}{dt_2} dt_1 dt_2 \\ &+ \frac{1}{2} \int_0^t \int_0^t G_B(t_1, t_2; t) \frac{d\varepsilon_v(t_1)}{dt_1} \frac{d\varepsilon_v(t_2)}{dt_2} dt_1 dt_2 \end{aligned}$$

Here,  $\varepsilon_v, e_{ij}^e, T, \dot{\varepsilon}_v, \dot{e}_{ij}^e, G_D$  and  $G_B$  are the volumetric strain, deviatoric elastic strain, temperature, volumetric strain rate, deviatoric strain rate, deviatoric kernel, and volumetric kernel, respectively.

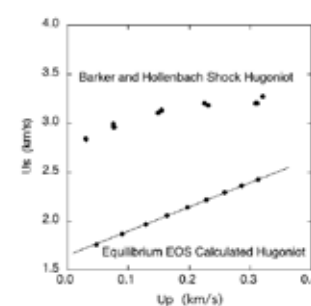
Determining functional expressions for  $G_D$  and  $G_B$ , and evaluating the resulting pressure, deviatoric stress, dissipation, and entropy is a long and rather complex process, the details of which are unimportant here. Finally, the model is implemented in a finite element code to perform simulations.

In the plate impact experiments of [4], 6.35mm PMMA plates impacted 6.35mm PMMA plates at various impact speeds. Figure 4 shows the experiment and our theoretical calculated shock profiles. Clearly the comparison is very good. Similarly, the theoretical shock Hugoniot now also agrees with that of Barker and Hollenbach [4]. The theory also shows that PMMA never reaches true equilibrium during the shock experiment.

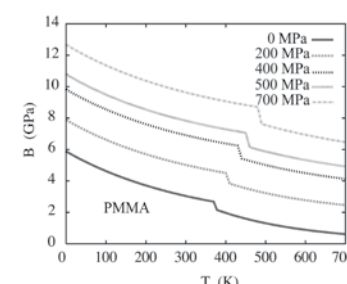
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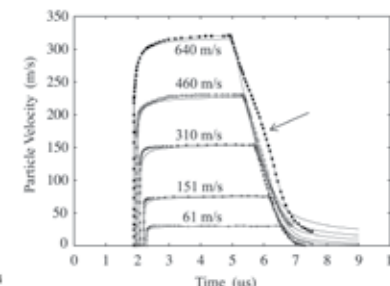
**Fig. 1. PMMA equilibrium Gibbs free energy.**



**Fig. 3. Shock Hugoniot from [2] and that calculated from the equilibrium EOS.**



**Fig. 2. PMMA equilibrium isothermal bulk modulus.**



**Fig. 4. PMMA shock profiles [2] (points) and from the theory (lines). Impact velocities are listed.**

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